

Effect of Nonproximate Atomic Substitution on Excited State Intramolecular Proton Transfer

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ABSTRACT: The central C atom of the OCCCO skeleton of the malonaldehyde molecule is replaced by N, and the effects upon the intramolecular H-bond and the proton transfer are monitored by *ab initio* calculations in the ground and excited electronic states. The H-bond is weakened in the singlet and triplet states arising from $n \rightarrow \pi^*$ excitation in both molecules, which is accompanied by a heightened barrier to proton transfer. ${}^3\pi\pi^*$ behaves in the same manner, but the singlet $\pi\pi^*$ state has a stronger H-bond and lower barrier. Replacement of the central C atom by N strengthens the intramolecular H-bond. Although the proton transfer barrier in the ground state of formimidol is lower than in malonaldehyde, the barriers in all four excited states are higher in the N-analog. The latter substitution also dampens the effect of the $n \rightarrow \pi^*$ excitation upon the H-bond and increases the excitation energies of the various states, particularly $\pi\pi^*$. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 129–138, 1998

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Introduction

In contrast to the thorough understanding of common ground state,^{1–5} those that occur in excited electronic states proton transfer (ESPT)

have received much less attention. Of particular interest has been the transfer of a proton across an intramolecular H-bond in molecules wherein the absorption occurs at a much higher frequency than the emission which follows the proton transfer. Systems such as these have found varied applications including lasers,^{6,7} and energy/data storage devices.^{8–10} One of the prime features common to many excited-state proton transfers is their rapidity, on the femto-to-nanosecond timescale.^{11–13} These fast transfers are commonly attributed to a process with a very low barrier or none at all.^{14,15} The change in the proton transfer barrier that ac-

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companies electronic excitation is of fundamental interest, as is the question as to which specific excited states can be expected to lead to such a barrier reduction.

The ESPT issue has drawn the attention of a number of recent *ab initio* studies.^{16–21} Much of this work has focused on the difference in energy between the two possible tautomers,^{22–24} with little attention devoted to the energy barriers separating the two minima, and the rapidity of the ESPT. A recent work offers promise that *ab initio* calculations are indeed useful in studying this problem. Although the large size of the [2,2'-bipyridine]-3,3'-diol molecule made high-level correlated calculations difficult,²³ the investigators noted a successful reproduction of the experimental finding of a stability reversal in the two chief tautomers, as well as solid agreement with experimental vibrational spectra.

Recent calculations in this laboratory have been chiefly concerned with molecules like malonaldehyde in which the intramolecular OH··O H-bond completes a five-membered ring of C and O atoms.^{25–27} This work has provided some insights into the properties of the ESPT within a molecule in the absence of complicating solvent effects, and free of interactions with a neighboring aromatic system. Replacement of one or more O atoms in malonaldehyde by N^{28–30} has enabled an elucidation of the dependence of the ESPT properties upon the nature of the atoms involved in the H-bond.

A question that has not been probed in any detail concerns the effect of changing the atoms that are not directly involved in the H-bond. The malonaldehyde molecule, for example, contains the intramolecular OH··O H-bond illustrated in Figure 1. Malonaldehyde contains three C atoms that connect the two oxygens. In the present communication, one of the three C atoms is replaced by nitrogen. (More specifically, to maintain the bond-

ing pattern, the central CH group is substituted by N.) It is the goal of this work to examine the perturbations introduced by this substitution into the H-bonding and proton transfer characteristics, not only of the ground state, but also of the first few excited states. Because this replacement takes place several atoms removed from the H-bonding site, it is anticipated that the changes might be subtle.

Methods

The two molecules of interest are illustrated in Figure 1 where the X refers to either a CH group or a N atom. With regard to nomenclature, malonaldehyde and formimidol are alternately referred to as OCCCO and OCNCO, respectively, to underscore their skeletal atomic makeup. This figure also displays the atomic labeling conventions used in this communication. The *d* and *a* subscripts are used to indicate the proton donor and acceptor atoms, respectively. The proton transfer passes through a symmetric transition state (TS), over an energy barrier, E^\ddagger . The endpoint of the transfer is pictured on the right side of Figure 1, and is symmetrically equivalent to the starting point equilibrium geometry. The fully planar geometries of all species were considered throughout.

The Gaussian-94 suite of programs³¹ was used to perform the calculations described here. Most calculations made use of the 6-31 + G** basis set.³² The geometries of the excited states were optimized using the CI singles (CIS) procedure,³³ as implemented in Gaussian.

Results

Table I lists the most important aspects of the equilibrium geometries of the two molecules of

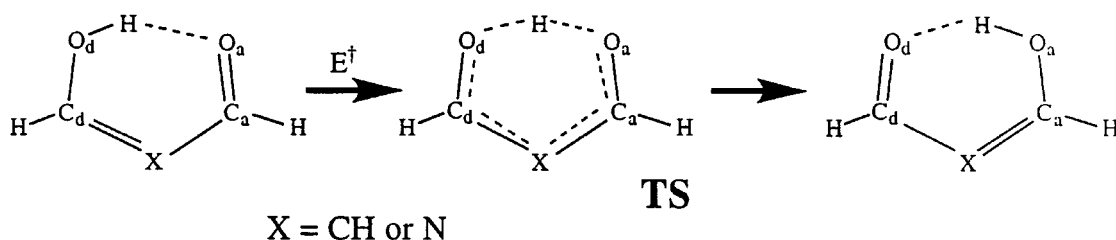


FIGURE 1. Atomic labeling schemes in malonaldehyde and formimidol. The *d* subscript refers to the proton donor atom in the equilibrium geometry on the left, and *a* to the acceptor. TS represents the transition state configuration for proton transfer.

interest, in the ground and various excited states. With regard first to the ground states, replacement of the central carbon atom by nitrogen shortens the CO bond of the donor group by some 0.01 Å, with a smaller contraction in the corresponding acceptor CO. Much more sizable are the reductions in the bonds to the central atom, amounting to 0.07 Å. The last three parameters on the right side of Table I deal explicitly with the intramolecular H-bond. The geometric parameters indicate the $C \rightarrow N$ replacement strengthens this $OH \cdots O$ interaction. The distance between the two oxygen atoms is reduced by 0.09 Å, coupled with a stretch of the bridging hydrogen away from the donor O by 0.003 Å. In either case, the H-bond contains an angular distortion of just under 30°, as indicated by the last column of Table I.

The effects of electronic excitation upon the geometries of the two molecules can be gleaned by comparison of the S_0 rows in Table I with the succeeding rows. In both cases, $n \rightarrow \pi^*$ excitation, whether to singlet or triplet, elongates the CO bonds. The C_dO_d stretch is in the range of 0.03–0.04 Å. The corresponding acceptor bond is also lengthened, and by a slightly greater amount. The bond connecting C_d to the central atom is slightly shortened by the $n \rightarrow \pi^*$ excitation. Discrepant behavior is noted in the XC_a bond. Whereas this bond is slightly lengthened in malonaldehyde in either the singlet or triplet, the opposite trend of a contraction is observed in formimidol, particularly in

$^1n\pi^*$. The H-bonds in the singlet and triplet $n\pi^*$ states are weaker than in the ground state. In both molecules, the interoxygen distance is lengthened by 0.2 Å, and $r(OH)$ contracted by 0.01 Å.

It has been noted previously that the singlet and triplet $\pi\pi^*$ states of malonaldehyde exhibit surprisingly different behaviors from one another.²⁷ This discrepancy is obvious in the pertinent rows of Table I where, for example, $r(O_dC_d)$ is shortened in the singlet versus the ground state, while this bond is elongated in the triplet. Replacement of the central C atom by nitrogen does not eliminate this contrasting behavior. In fact, these discrepancies between the singlet and triplet occur in the H-bond as well. This interaction is apparently strengthened in the $^1\pi\pi^*$ state, and weakened in the triplet. The same is true in formimidol, although the changes are not as extreme as in malonaldehyde.

The latter geometric signs of H-bond strength are confirmed by the energetic data in Table II. Considering the first row of that table, replacement of the central C by N weakens the H-bond by a small amount (this effect is opposite to that suggested by the geometries). This order is reversed in the two $n\pi^*$ states when the H-bond appears to be stronger in formimidol. But, perhaps more importantly, the patterns within the various states that were noted in malonaldehyde remain largely in force in formimidol as well. The bond weakening resulting from $n \rightarrow \pi^*$ excitation occurs in both molecules, although not as extreme in

TABLE I.
Optimized Geometries (Angstroms and Degrees) of Complexes in Figure 1, Calculated with 6-31 + G Basis Set.**

	O_dC_d	C_dX^a	XC_a	C_aO_a	$O_d \cdots O_a$	O_dH	$\theta(O_aO_dH)$
OCCCCO							
S_0	1.311	1.345	1.453	1.208	2.689	0.956	27.8
$^1\pi\pi^*$	1.293	1.451	1.423	1.255	2.577	0.983	21.8
$^3\pi\pi^*$	1.351	1.460	1.425	1.223	2.826	0.946	29.7
$^1n\pi^*$	1.341	1.334	1.462	1.258	2.905	0.945	34.3
$^3n\pi^*$	1.346	1.329	1.467	1.255	2.948	0.943	35.2
OCNCO							
S_0	1.300	1.276	1.381	1.204	2.602	0.959	29.4
$^1\pi\pi^*$	1.297	1.385	1.342	1.256	2.579	0.973	26.0
$^3\pi\pi^*$	1.348	1.360	1.350	1.239	2.770	0.944	33.5
$^1n\pi^*$	1.338	1.271	1.357	1.248	2.804	0.949	36.0
$^3n\pi^*$	1.341	1.263	1.374	1.250	2.810	0.946	37.3

^aX is either C or N.

TABLE II.
Hydrogen-Bond Energies^a (Kilocalories per Mole)
Calculated at CIS / 6-31 + G Level.**

	OCCCO	OCNCO
S_0	14.1	12.3
$^1\pi\pi^*$	23.6	14.3
$^3\pi\pi^*$	6.7	4.1
$^1n\pi^*$	2.3	6.0
$^3n\pi^*$	0.5	1.8

^aDefined as difference in energy between equilibrium geometry and rotamer with bridging H rotated 180° with forced planarity.

formimidol. The $\pi \rightarrow \pi^*$ excitation, on the other hand, weakens the H-bond in the case of the triplet, but is strengthened in the singlet. Again, the changes are more moderate in formimidol.

Some insights into the fundamental source of the different behavior of malonaldehyde and formimidol may be gleaned by inspection of the relevant MOs of the two systems. The n orbital (second highest occupied molecular orbital) of the two systems, is illustrated in Figure 2.* In comparison to malonaldehyde, there appears to be stronger bonding character between the O_d and C_d atoms in formimidol. The loss of this stronger bond helps explain the greater elongation in this bond caused by the $n \rightarrow \pi^*$ excitation in formimidol. Whereas there appears to be clear evidence of a bond between the central atom and C_a in malonaldehyde, the corresponding MO in formimidol resembles more of a nonbonding p -type orbital on the N atom. Consequently, the bond is lost in malonaldehyde, resulting in a longer CC_a bond, in contrast to this same NC_a bond in formimidol, which is shortened by the same excitation. Whereas the n MOs of malonaldehyde and formimidol exhibit certain differences, the same is not true of the highest occupied π orbitals. Inspection of the two indicates no significant differences in shape or extent.

The energies required to elevate each system from its ground state to each of the various excited states are listed in Table III. The columns labeled as vertical refer to excitations in which the geometry of the excited as well as the ground state is

*The excited states do not represent "pure" excitations from one occupied MO to a single vacant MO, but are better described as a linear combination of excitations, each from an occupied MO to a vacant one, of pertinent symmetry. For most states, the collection is derived largely from a single occupied MO, but several different vacant orbitals typically make significant contributions.

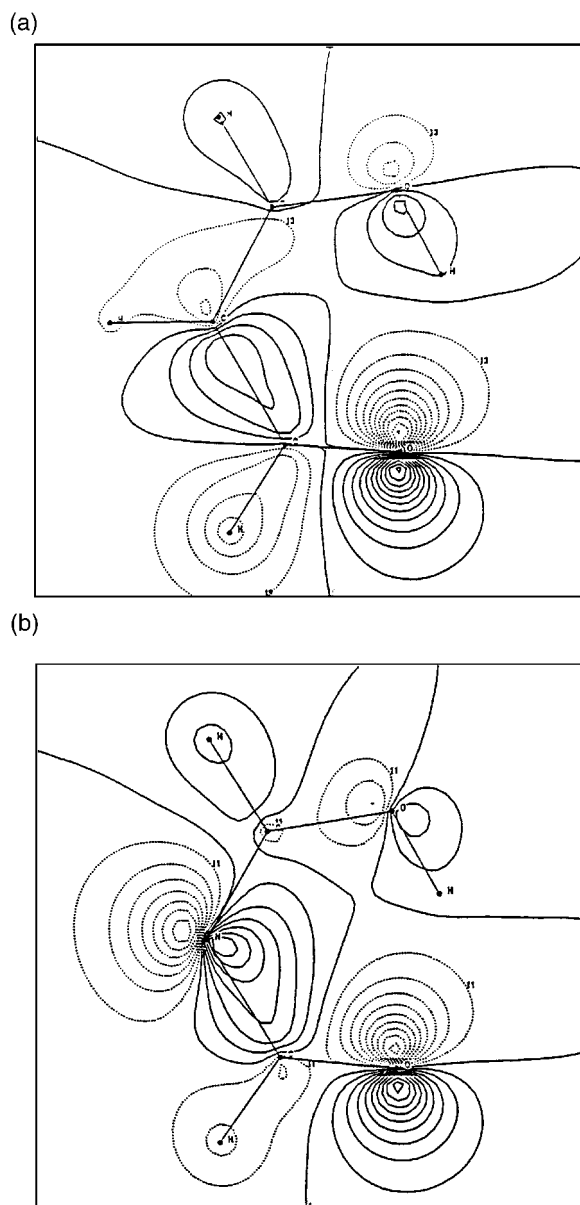


FIGURE 2. Contour plots of highest occupied n orbitals in equilibrium geometries of (a) malonaldehyde and (b) formimidol, plotted in the molecular plane. Regions of positive and negative amplitude are denoted by solid and broken contour lines, respectively. The molecules are oriented so that the proton donor group is at the top and the acceptor near the bottom.

frozen in the optimized geometry of the ground state. The adiabatic excitation energies in the succeeding columns permit the excited state to adopt its most stable geometry following the excitation. This relaxation of the upper state leads to adiabatic excitation energies which are smaller than the vertical quantities. The relaxation energy varies from

TABLE III.
Excitation Energies (Kilocalories per Mole) Calculated with 6-31 + G Basis Set.**

	Vertical		Adiabatic			
	CIS		CIS		MP2	
	OCCCO	OCNCO	OCCCO	OCNCO	OCCCO	OCNCO
$^1\pi\pi^*$	144.6	168.5	126.1	157.4	130.6	151.0
$^3\pi\pi^*$	80.4	108.5	56.3	96.5	109.4	142.6
$^1n\pi^*$	121.1	128.2	110.3	118.5	126.9	124.1
$^3n\pi^*$	106.7	115.3	94.5	107.2	123.0	125.7

one state to the next and is largest for the $\pi\pi^*$ states. Replacement of the central carbon by nitrogen reduces the relaxation energy in all four states considered.

In both systems, the $^1\pi\pi^*$ excitation energy is particularly large, as much as 70 kcal/mol higher than for the corresponding triplet. The singlet–triplet separation in the $n\pi^*$ pair of states is far smaller. As a result, the latter two states fall in between the singlet and triplet $\pi\pi^*$ states. The state ordering for the two molecules is:

$$^3\pi\pi^* < ^3n\pi^* < ^1n\pi^* < ^1\pi\pi^* \quad (1)$$

The C \rightarrow N substitution raises all excitation energies, especially those of the $\pi\pi^*$ states, by 8–40 kcal/mol.

The last two columns of Table III provide information concerning the effect of electron correlation upon the excitation energies. The values reported there refer to the difference in energy between the ground and excited states at the MP2 level, with geometries of both optimized at the SCF and CIS levels, respectively. It should be noted that, with the exception of the $^1\pi\pi^*$ state of formimidol, all excitation energies are increased by inclusion of electron correlation. This increase is particularly large in magnitude for the $^3\pi\pi^*$ state, so much so that the latter state is elevated above the singlet and triplet $n\pi^*$ states at the MP2 level.

PROTON TRANSFER BARRIERS

The energy barrier to proton transfer is defined as the difference in energy between the optimized geometry of each state and the transition state wherein the bridging hydrogen is midway between the two oxygen atoms. As may be seen in the first row of Table IV, the replacement of the central carbon by nitrogen reduces the transfer barrier by a small amount at the uncorrelated level from 10.3 to 8.9 kcal/mol. However, the opposite

TABLE IV.
Proton Transfer Barriers (Kilocalories per Mole) Calculated with 6-31 + G Basis Set.**

	CIS		MP2	
	OCCCO	OCNCO	OCCCO	OCNCO
S_0	10.3	8.9	2.3	3.3
$^1\pi\pi^*$	4.3	6.3	−5.8	−3.7
$^3\pi\pi^*$	21.1	24.1	−0.6	0.3
$^1n\pi^*$	23.7	29.2	−2.8	9.8
$^3n\pi^*$	28.4	30.1	0.9	9.3

pattern is noted in the excited states wherein the barriers in formimidol are uniformly higher than in malonaldehyde. This difference is around 2 kcal/mol, although it reaches as much as 5.5 kcal/mol for the $^1n\pi^*$ state. For both molecules, the singlet and triplet $n\pi^*$ states exhibit high barriers, with the singlet barrier slightly the lower of the two. The $\pi\pi^*$ barriers are less consistent: the singlet lowers the barrier, whereas an increase is observed in the triplet.

As may be witnessed by the following two columns of Table IV, adding correlation lowers each barrier, consistent with prior calculations.^{34–37} At the MP2 level, the formimidol barriers are larger than in malonaldehyde, in all states including S_0 .

It has been noted on numerous occasions in the past that the proton transfer barrier bears a strong relationship to the length of the H-bond. This relationship is illustrated in Figure 3 for the two molecules of interest here. The malonaldehyde barriers are plotted as a function of $R(\text{O} \cdots \text{O})$ for the various electronic states, labeled by the OCCCO designation. The barrier appears to vary approximately linearly with interoxygen distance, such that each lengthening by 0.1 Å is accompanied by a barrier increase of 6.4 kcal/mol. The relationship is also close to linear for formimidol, as indicated by the OCNCO curve in Figure 3. The

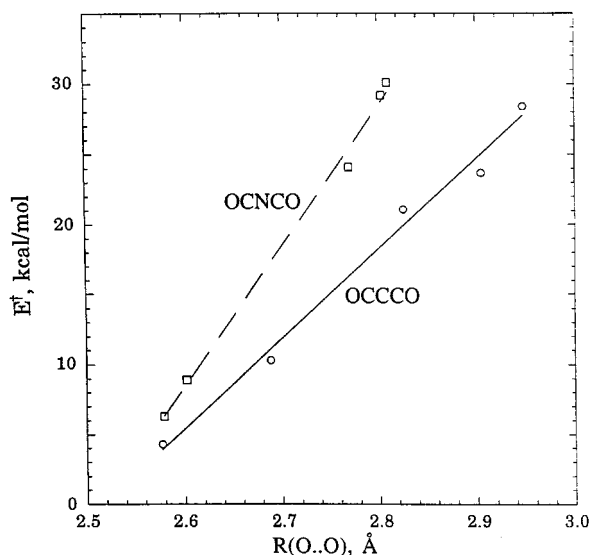


FIGURE 3. CIS proton transfer barriers as a function of interoxygen separation. The two sets of data are fit separately by the straight lines indicated. Correlation coefficients are above 0.99 in both cases.

sensitivity of the barrier to $R(\text{O} \cdots \text{O})$ is enhanced in this system relative to malonaldehyde; the same stretch of 0.1 Å raises the barrier by 10.0 kcal/mol. Figure 3 emphasizes that, given equivalent $R(\text{O} \cdots \text{O})$, the substitution of the central carbon atom by nitrogen produces an increase in the barrier in all states, especially those with long intramolecular H-bond.

Strengthened H-bonds are typically associated not only with shorter $R(\text{O} \cdots \text{O})$ but also a stretch of the bridging hydrogen away from the donor oxygen atom. The connection between $r(\text{OH})$ and the transfer barrier is exhibited in Figure 4. As expected, the stretches in this bond mark a lower transfer barrier. With regard to the specifics of the pattern, a sharp dropoff in the barrier is observed as $r(\text{OH})$ begins to stretch, but this sensitivity declines as the barrier diminishes toward zero. It is notable that, unlike the case of $R(\text{O} \cdots \text{O})$ in Figure 3, where the data for malonaldehyde and formimidol fall along different lines, the barriers for the two systems intermix when plotted against $r(\text{OH})$.

The geometry changes that result from the half-transfer of the proton provide additional information about the nature of the proton transfer process. These changes are reported in Table V as the difference between the equilibrium geometry listed in Table I, and the structure of the transition state

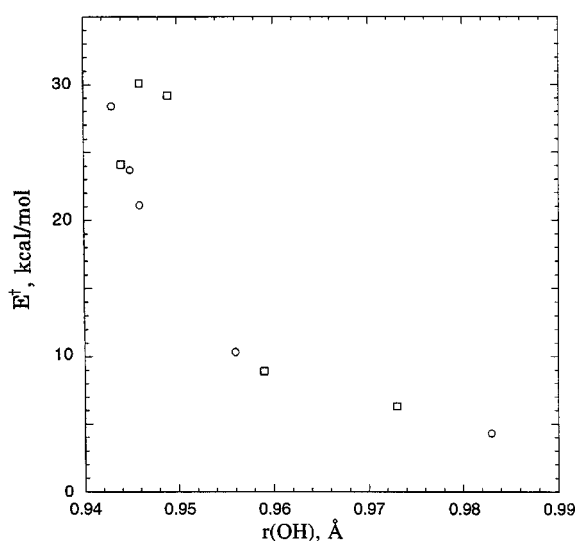


FIGURE 4. CIS proton transfer barriers as a function of equilibrium value of $r(\text{OH})$. The values for the **OCCCO** and **OCNCO** systems are indicated by the circles and squares, respectively.

along the proton transfer coordinate. For example, the first data entry of Table V indicates that the motion of the proton toward the middle of the H-bond causes the O_dC_d bond of malonaldehyde to contract by 0.05 Å. This shortening is observed not only in the ground state but in the four excited states as well. The smallest contraction is associated with the $^1\pi\pi^*$ state and the largest for the corresponding triplet. This same pattern is repeated for formimidol. The CO bond on the acceptor side of the molecule is lengthened by the approach of the proton, in amounts comparable to the contraction in $r(\text{O}_d\text{C}_d)$. The bonds to the central atom follow different trends. The C_dC bond in malonaldehyde is lengthened in the ground state as well as the two $n\pi^*$ states, as compared to a shortening in $\pi\pi^*$. This pattern is repeated in the C_dN bond of formimidol, although the changes tend to be somewhat smaller in magnitude. The changes observed in the XC_d bond are roughly mirror images of C_dX , increasing when the latter decrease, and vice versa.

Much larger in magnitude are the reductions that occur in the $\text{O} \cdots \text{O}$ distance upon half-proton transfer. This contraction varies from 0.2 Å in the $^1\pi\pi^*$ states to some 0.6–0.7 Å in $n\pi^*$. This sort of H-bond shortening has been noted on numerous occasions, both for intramolecular and intermolecular H-bonds in their ground state^{38–42} as well as

TABLE V.
Changes in Geometries (Angstroms and Degrees) of Complexes in Figure 1 Resulting from Formation of
Transition States to Proton Transfer.

	$O_d C_d$	$C_d X$	$X C_a$	$C_a O_a$	$O_d \cdots O_a$	$O_d H$	$\theta(O_a O_d H)$
OCCCC							
S_0	-0.054	0.050	-0.058	0.049	-0.366	0.233	-15.5
$^1\pi\pi^*$	-0.020	-0.014	0.014	0.018	-0.210	0.224	-10.4
$^3\pi\pi^*$	-0.067	-0.043	-0.008	0.061	-0.475	0.252	-18.6
$^1n\pi^*$	-0.048	0.056	-0.072	0.035	-0.636	0.226	-19.9
$^3n\pi^*$	-0.058	0.063	-0.075	0.033	-0.675	0.230	-20.9
OCNCO							
S_0	-0.051	0.051	-0.054	0.045	-0.297	0.228	-15.5
$^1\pi\pi^*$	-0.023	-0.020	0.023	0.018	-0.225	0.234	-13.3
$^3\pi\pi^*$	-0.066	-0.015	-0.005	0.043	-0.433	0.253	-21.0
$^1n\pi^*$	-0.043	0.045	-0.041	0.047	-0.562	0.219	-19.8
$^3n\pi^*$	-0.051	0.054	-0.057	0.040	-0.564	0.223	-21.1

excited states.^{20,43} In fact, it is commonly observed that the greatest amount of H-bond contraction is associated with weaker H-bonds, with the highest transfer barriers. This pattern is borne out by the ground and excited state data reported here as well. The nearly linear relationship between the equilibrium H-bond length and its degree of contraction upon half-proton transfer is exhibited in Figure 5. The correlation coefficient computed for this relationship between R and ΔR is 0.98, characterized by the broken line in Figure 5. The slope of the fitting line suggests that each increment of 0.1 Å in the equilibrium H-bond length is associated with an increase in the transfer-induced contraction of 0.12 Å. With the exception of the $^1\pi\pi^*$ state, the H-bond contractions are smaller when the central C of malonaldehyde is replaced by N. Nonetheless, the data for the two molecules fall along the same line in Figure 5.

The last two columns in Table IV refer to the proton transfer barriers computed at the MP2 level, using geometries optimized by CIS. Consistent with prior findings,⁴⁴⁻⁴⁶ electron correlation lowers these transfer barriers. The negative values reported for some of these barriers indicate that the MP2 energy of the transition state geometry is lower than that of the equilibrium structure, both optimized at the CIS level. This sort of collapse of the barrier at the MP2 level has been noted in other studies of excited states.^{20,43} Like the CIS data, the MP2 barriers are higher for formimidol than for malonaldehyde for most of the pertinent states. However, the quantitative aspects of the

CIS and MP2 barriers are quite distinct for the most part.

Discussion and Summary

Just as in the case of ground state processes, the results here contain indications of a strong rela-

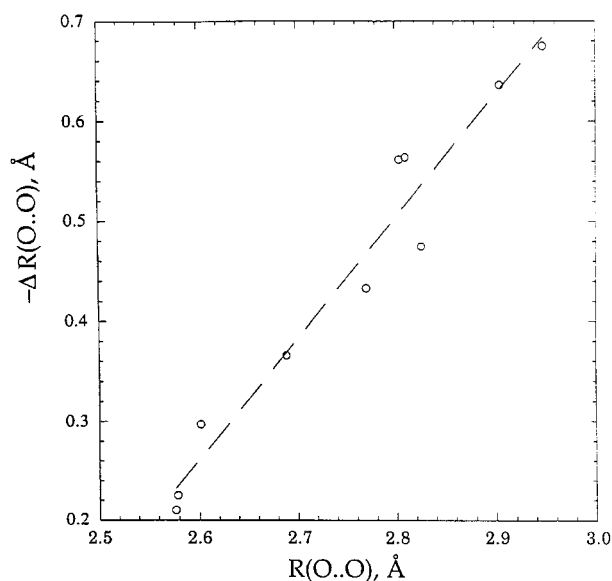


FIGURE 5. Relationship between the computed equilibrium H-bond length $R(O \cdots O)$ in the various electronic states of the two systems, and the amount that this distance contracts as a result of motion of the bridging hydrogen to the $O \cdots O$ midpoint.

tionship between the height of the barrier to proton transfer and the strength of the intramolecular hydrogen bond. To elucidate some of the fundamental causative factors, it is instructive to examine the electronic redistributions that accompany the various excitations, especially those intimately connected with the H-bond.

The nonbonding (n) MOs from which the $n\pi^*$ excitations are derived appear to contain a high electron density on the proton-acceptor oxygen atom O_a . This density is situated in a region where it is able to accommodate the bridging hydrogen, helping to form the H-bond. The excitation of an electron out of this MO is thus expected to weaken the H-bond, which is confirmed by the energetic and geometric data reported above. A quantitative measure of the density shift is the charge assigned to the O_a atom, and how it changes upon excitation. The changes in Mulliken charge of this atom that are associated with excitation to each of the pertinent excited states are listed in Table VI. The electron density shifts away from the proton acceptor atom suggested by inspection of the MOs are confirmed by the large positive values listed in the last two rows of Table VI for malonaldehyde. The charge changes in the nitrogen-containing analog are quite a bit smaller in magnitude, as though the intervening N atom somehow insulates the acceptor oxygen atom from loss of density. This finding is especially intriguing because inspection of the pertinent MOs of the two molecules does not show evidence of strong differences in the vicinity of the O_a atom.

The two $\pi\pi^*$ states also exhibit interesting changes in the charge of O_a . Whereas some density is lost from the triplet, there is a small buildup on this atom in the singlet. The former loss of density is considerably larger in the formimidol molecule. The presence of the nitrogen also lessens the buildup that occurs in the $^1\pi\pi^*$ state. One may

summarize the effect of the replacement of the central CH by nitrogen to be a lessening of the density reduction in the $n\pi^*$ states, and an enhancement in the density loss in the $\pi\pi^*$ states.

The charge changes listed in Table VI are only crude single-parameter measures of the density around the O_a atom. The Mulliken atomic charge represents a sum of the σ and π densities, and contains an implicit arbitrary partitioning of density between this atom and its neighbors. For that reason, close correspondence between these charges and energetic measures of H-bond strength and transfer barrier is not necessarily expected. In fact, the charge changes stand in some contrast to the transfer barriers in Table IV. For example, the charge changes are less positive for formimidol than for malonaldehyde in the two $n\pi^*$ states, but more positive in singlet and triplet $\pi\pi^*$. In contrast, the barriers of all four states are higher for the nitrogen-substituted species.

There have been other calculations that lead to questions about the ability of MP2 treatment of correlation, following a CIS calculation, to properly handle ESPT processes.^{47, 48} It is for this reason that the MP2 barriers of the excited states have not been emphasized in this report. In any case, the CIS treatment, used for optimizing the geometries of our excited state species, would appear to yield reasonable results.^{49–51} The most appropriate means of computing electron correlation in excited states such as these requires further scrutiny and is under current investigation in this laboratory.

The malonaldehyde molecule and its nitrogen-containing analog, formimidol, have much in common. A ring structure is present in both, culminating in an intramolecular H-bond connecting the two O atoms. $n \rightarrow \pi^*$ excitation weakens this H-bond, and lengthens the CO bonds on both sides of the molecule. An important result of this excitation is enlarged proton transfer barriers. Whereas the triplet $\pi\pi^*$ state follows much the same pattern as the $n\pi^*$ cases, the $^1\pi\pi^*$ state behaves in an opposite fashion, associated with a strengthened intramolecular H-bond and lowered transfer barrier.

Both systems have the same ordering of the excited states. The two triplets lie below the singlets; $^3\pi\pi^*$ is the lower of the two triplets and $^1n\pi^*$ is the more stable of the singlets. The proton transfer barriers in the $n\pi^*$ states are quite a bit higher than in the ground state, as is the case of $^3\pi\pi^*$. $^1\pi\pi^*$ is exceptional in that the barrier is

TABLE VI.
Changes in Mulliken Charge of O_a Caused by Indicated Excitation from Ground State.^a

	OCCCO	OCNCO
$^1\pi\pi^*$	−0.040	−0.003
$^3\pi\pi^*$	0.090	0.205
$^1n\pi^*$	0.368	0.146
$^3n\pi^*$	0.424	0.284

^aNegative sign corresponds to a loss of electron density as a result of excitation; charges in S_0 are −0.598, and −0.581 for OCCCO and OCNCO, respectively.

lower than that of the ground state. There is a strong relationship between this transfer barrier and the interoxygen distance in the equilibrium geometry. The same is true of the $r(\text{OH})$ bond length which correlates well with the transfer barrier. Half transfer of the bridging hydrogen is accompanied by a marked reduction in the H-bond length $R(\text{O} \cdots \text{O})$. This contraction parallels other facets of the H-bond, such as the equilibrium value of $R(\text{O} \cdots \text{O})$ or H-bond energy.

More than the similarities, the differences between OCCCCO and OCNCO are perhaps the more interesting. The nitrogen substitution shortens the skeletal bonds in the equilibrium geometries of the ground state. These contractions are most notable for the bonds involving the central atom, but occur as well in both of the CO bonds. The N-analog also contains a stronger H-bond between the two O atoms. The $n \rightarrow \pi^*$ excitations do not have quite so much of an effect upon the intramolecular H-bond in formimidol as in malonaldehyde, although the barriers are raised more in the former molecule by this excitation. The nature of the relevant highest occupied n MO of the two molecules indicates stronger bonding character in the CO bond of the donor group of formimidol, as compared to malonaldehyde. The bond between the central C atom in malonaldehyde and its neighboring C_α atom, is largely absent in the N-analog. These two differences help to account for the differing bond length alterations observed in the two molecules.

The replacement of the central CH by nitrogen has the effect of raising the excitation energies of the four excited states. The amount of this increase is particularly large for the $\pi\pi^*$ states, reaching as much as 40 kcal/mol. Although the proton transfer barrier in the ground state of formimidol is lower than in malonaldehyde, the barriers in all four excited states are higher in the N-analog. In other words, the N-substitution enhances the effect of electronic excitation upon the transfer barriers. For a given interoxygen distance, the transfer barriers are higher in formimidol than in malonaldehyde. The former molecule also exhibits somewhat smaller $R(\text{O} \cdots \text{O})$ contractions upon half-proton transfer.

The system considered in the present study is symmetric in that the two wells in the transfer potential are identical in energy. Past work in this laboratory^{29,30,52} addressed the issue of asymmetric systems, and the manner in which the relative

energies of the two wells are affected by electronic excitation. This type of analysis will be extended to more complex systems shortly.

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